

# PATENT SPECIFICATION

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## (54) PROCESS FOR THE PRODUCTION OF METHACRYLIC ACID

(71) We, JAPAN SYNTHETIC RUBBER COMPANY LIMITED, of 1, Kyobashi-1-chome, Chuo-ku, Tokyo, Japan, a Body Corporate organised and existing under the laws of Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to catalysts which are useful in the production of methacrylic acid from methacrolein by gas phase catalytic oxidation and specifically to such a process using these catalysts.

Various types of catalyst and process have previously been proposed for the production of acrylic acid or methacrylic acid by the gas phase catalytic oxidation of acrolein or methacrolein, respectively, but these processes generally have disadvantages which render them unsuitable for industrial application. Even if the catalysts give good results, they are often not consistently reproducible and thus satisfactory results cannot always be assured.

We have now surprisingly found that a catalyst containing four metallic components (molybdenum, nickel, vanadium and tungsten), as essential components, and optionally certain other metals, in the form of a compound oxide, is suitable for the gas phase catalytic oxidation of methacrolein to methacrylic acid, in high yield and with good reproducibility.

Thus, the present invention consists in a process for the preparation of methacrylic acid by the gas phase oxidation of methacrolein with molecular oxygen in the presence, as catalyst, of a composition comprising a compound oxide of molybdenum, nickel, vanadium and tungsten.

Optionally, the oxide additionally comprises

one or more of the alkali metals: lithium, sodium, potassium, rubidium and caesium. Also, in addition to the four essential metals (Mo, Ni, V and W) and the alkali metals, the compound oxide optionally comprises one or more of the elements thallium, zirconium, chromium, cobalt, iron, niobium, titanium, zinc, indium and tantalum. In a preferred embodiment of the invention, the compound oxide contains the metals in the ratios (expressed as gram atoms), Mo:Ni:V:W:M:X of 20:1 — 20:0.1 — 10:0.1 — 10:0 — 5:0 — 10 and preferably 20:7 — 13:0.5 — 2:0.5 — 2:0 — 0.5:0 — 2, where M represents one or more of the alkali metals, lithium, sodium, potassium, rubidium and caesium, and X represents one or more of the metals, thallium, zirconium, chromium, cobalt, iron, niobium, titanium, zinc, indium and tantalum.

The preferred alkali metals are potassium, rubidium and caesium.

We have surprisingly found that the catalytic gas phase oxidation of methacrolein to methacrylic acid takes place with considerably increased yields when the catalyst is a compound oxide of molybdenum, nickel, vanadium and tungsten compared with the yields if the catalyst simply consists of a compound oxide of molybdenum, nickel and vanadium or a compound oxide of molybdenum, nickel and tungsten. Furthermore, if the compound oxide contains, in addition to the four essential metals, one or more of the alkali metals, the yield of the desired methacrylic acid is still further increased. The further addition of one or more of the metals thallium, zirconium, chromium, cobalt, iron, niobium, titanium, zinc, indium and tantalum (in addition to molybdenum, nickel, vanadium, tungsten and one or more of the alkali metals) gives even better results in terms of the conversion of methacrolein, selectivity to desired methacrylic acid and yield of methacrylic acid.

The catalytic compositions used in the process of the invention can be prepared by techniques well known in the production of compound oxides, including: simple mixing of the oxides; evaporation to dryness of solutions containing the requisite elements; or coprecipitation. Thus, it is possible to produce the compound oxides starting from the metals themselves, from metallic salts, metallic acids or metallic bases, provided that these can be finally converted to oxides with ease during calcination of the catalytic composition. In general, we prefer to start from nitrates, organic acid salts, ammonium salts and hydroxides.

After producing the mixture of oxides by the techniques described above, it is desirable to calcine this mixture in an air stream at a temperature of from 300° C. to 700° C., preferably from 350° C. to 600° C., for a period of from 2 to 40 hours, preferably from 5 to 20 hours.

The catalytic composition can be used in the process of the invention without any carrier, but we prefer that it should be used with a carrier. Carriers suitable for use in the present invention include those frequently used in oxidation reactions, such as silica, alumina, e.g. in the form of fused alumina grains such as those sold under the registered Trade Mark "Alundum", silicon carbide, pumice, and aluminium sponge, preferred carriers being silicon carbide, alumina and silica. The amount of the compound oxide deposited on the carrier depends on the procedure employed for preparing it, but in general we prefer to deposit from 1 to 1000 parts by weight of compound oxide on 100 parts by weight of the carrier.

In the process of the invention, methacrolein, molecular oxygen and preferably steam, optionally with an inert gas, are passed over

the catalytic composition of the invention at an elevated temperature and the methacrolein is catalytically oxidised to methacrylic acid. The conditions employed for this process depend on the catalytic ability of the composition and such conditions as reaction temperature, contact time and concentration of methacrolein are generally closely inter-related. In general, however, preferred conditions are as follows:

Reaction temperature: 250° C. to 500° C., preferably from 300° C. to 400° C.;

Reaction pressure: either superatmospheric or subatmospheric pressure may be employed, but the reaction is most conveniently carried out at atmospheric pressure;

Contact time: 0.1 to 20 seconds, preferably from 1 to 10 seconds;

Molar ratio of methacrolein: oxygen is from 1:05 to 1:5.0, preferably from 1:1 to 1:4;

Molar ratio of methacrolein to steam, if used, is from 1:1 to 1:50, preferably from 1:3 to 1:30.

Air is the most convenient source of oxygen, but pure oxygen, or a mixture of oxygen with an inert gas such as nitrogen, carbon dioxide, helium, argon or a saturated hydrocarbon (e.g. methane, ethane, propane or butane), can be used.

The reaction product can be separated and recovered by conventional procedures, e.g. condensation, extraction, distillation or other appropriate techniques.

The invention is further illustrated with reference to the following Examples. In the Examples, analysis was carried out by gas chromatography and the terms "conversion" (as applied to methacrolein), "selectivity" (for the formed methacrylic acid) and "one-pass yield" (of the formed methacrylic acid) are defined by the following formulae:

$$\text{Conversion of methacrolein (mole \%)} = \frac{\left[ \begin{array}{c} \text{Supplied} \\ \text{methacrolein} \\ \text{(moles)} \end{array} \right] - \left[ \begin{array}{c} \text{Unreacted} \\ \text{methacrolein} \\ \text{(moles)} \end{array} \right]}{\text{Supplied methacrolein (moles)}} \times 100$$

$$\text{Selectivity to methacrylic acid (mole \%)} = \frac{\text{Methacrylic acid formed (moles)}}{\left[ \begin{array}{c} \text{Supplied} \\ \text{methacrolein} \\ \text{(moles)} \end{array} \right] - \left[ \begin{array}{c} \text{Unreacted} \\ \text{methacrolein} \\ \text{(moles)} \end{array} \right]} \times 100$$

$$\text{One pass yield of methacrylic acid (mole \%)} = \frac{\text{Methacrylic acid formed (moles)}}{\text{Supplied methacrolein (moles)}} \times 100$$

$$= \text{Conversion} \times \text{Selectivity} \times \frac{1}{100}$$

## EXAMPLE 1.

55.2 g. of ammonium paramolybdate,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ , 1.8 g. of ammonium metavanadate,  $\text{NH}_4\text{VO}_3$ , and 4.1 g. of ammonium paratungstate,  $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}$ , were dissolved, respectively, in 500 ml., 200 ml., and 400 ml. of distilled water; the resulting solutions were then mixed together. An aqueous solution containing 45.5 g. of nickel nitrate,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , dissolved in 200 ml. of distilled water was added to the resulting mixed solution and the mixture was then stirred. Aqueous ammonia was then added dropwise, with stirring, to the solution to raise the pH of the solution to about 8. A precipitate was formed on adding the aqueous ammonia, and, after adding 300 g. of silicon carbide, the resulting suspension was evaporated to dryness over a water bath, to deposit the catalyst components on the silicon carbide. After this, the resulting supported catalyst was dried at 130° C. for 10 hours and then

calcined at 500° C. for 7 hours in an air stream.

25 ml. of the resulting supported catalyst were placed in a Pyrex (registered Trade Mark) glass reactor having an inner diameter of 20 mm. and a feedstock gas comprising methacrolein, air and steam in a molar ratio of 2.9:22.0:75.1 was passed through the reactor at 370° C. and a space velocity of 1000  $\text{hr}^{-1}$  (contact time 3.6 seconds). The results are shown in Table 1.

## EXAMPLES 2-6.

Catalysts having different atomic ratios of the four metallic compounds, molybdenum, nickel, vanadium and tungsten, were prepared in the manner described in Example 1 and methacrolein was oxidised under the same reaction conditions as are described in Example 1.

The results are also shown in Table 1. The amounts of the catalyst components are specified as atomic ratios.

TABLE 1

Example No.	Catalyst			Conversion of methacrolein (%)	Selectivity to methacrylic acid (%)	One-pass yield of methacrylic acid (%)
	Mo	Ni	V W			
1	20	10	1 1	72.6	58.8	42.7
2	20	10	0.5 0.5	64.1	62.7	40.3
3	20	10	2 1	70.5	58.9	41.5
4	20	10	3 1	68.7	57.0	39.2
5	20	15	1 1	65.9	60.4	39.8
6	20	7	1 1	67.2	61.6	41.4

## EXAMPLES 7—11.

Catalysts containing molybdenum, nickel, vanadium, tungsten and an alkali metal were prepared in the manner described in Example 1, except that a predetermined quantity of an aqueous solution of an alkali metal salt was added to the solution after addition of the

aqueous solution of nickel nitrate. Methacrolein was oxidised using the same reaction conditions as are described in Example 1.

The results are shown in Table 2 in which, as in the subsequent Tables, the relative amounts of the catalyst components are expressed as atomic ratios.

TABLE 2

Example No.	Catalyst	Conversion of methacrolein (%)	Selectivity to methacrylic acid (%)	One-pass yield of methacrylic acid (%)
7	$\text{Mo}_{20}\text{Ni}_{10}\text{V}_1\text{W}_1\text{Li}_{10.2}$	67.3	66.4	44.7
8	" $\text{Na}_{0.2}$	65.8	65.4	43.0
9	" $\text{K}_{0.2}$	68.2	66.5	45.3
10	" $\text{Rb}_{0.2}$	67.7	65.3	44.2
11	" $\text{Cs}_{0.2}$	69.1	66.3	45.8

## EXAMPLE 12.

A catalyst containing molybdenum, nickel, vanadium, tungsten, caesium and cobalt was prepared as described in Example 1, except that predetermined quantities of an aqueous solution of caesium nitrate and an aqueous solution of cobalt nitrate were added to the solution after addition of the nickel nitrate. Methacrolein was then oxidised using the re-

action conditions described in Example 1. The results are shown in Table 3.

## EXAMPLES 13—21.

Example 12 was repeated, except that the cobalt was replaced by, respectively, titanium, chromium, iron, zinc, zirconium, niobium, indium, tantalum and thallium. The results are also shown in Table 3.

TABLE 3

Example No.	Catalyst	Conversion of methacrolein (%)	Selectivity to methacrylic acid (%)	One-pass yield of methacrylic acid (%)
12	$\text{Mo}_{20}\text{Ni}_{10}\text{V}_1\text{W}_1\text{Cs}_{0.2}\text{Co}_1$	68.4	68.0	46.5
13	" $\text{Ti}_1$	72.1	65.4	47.1
14	" $\text{Cr}_1$	68.7	67.0	46.0
15	" $\text{Fe}_1$	66.9	67.1	44.9
16	" $\text{Zn}_1$	70.5	65.7	46.3
17	" $\text{Zr}_1$	67.5	70.2	47.3
18	" $\text{Nb}_1$	70.5	65.5	46.1
19	" $\text{In}_1$	66.1	70.3	46.6
20	" $\text{Ta}_1$	66.9	67.6	45.2
21	" $\text{Ti}_{0.2}$	68.5	75.0	51.5

## EXAMPLES 22-26.

Catalysts having the following compositions were prepared in the manner described in Example 12:

$\text{Mo}_{20}\text{Ni}_{10}\text{V}_1\text{W}_1\text{Li}_{0.2}\text{Ti}_{0.2}$ ;  
 $\text{Mo}_{20}\text{Ni}_{10}\text{V}_1\text{W}_1\text{Na}_{0.2}\text{Co}_1$ ;  
 $\text{Mo}_{20}\text{Ni}_{10}\text{V}_1\text{W}_1\text{K}_{0.2}\text{In}_1$ ;  
 $\text{Mo}_{20}\text{Ni}_{10}\text{V}_1\text{W}_1\text{K}_{0.2}\text{Ti}_{0.2}$ ; and  
 $\text{Mo}_{20}\text{Ni}_{10}\text{V}_1\text{W}_1\text{Rb}_{0.2}\text{Nb}_1$ .

Methacrolein was then oxidised using these catalysts under the reaction conditions described in Example 1.

The results are shown in Table 4.

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## EXAMPLES 27 and 28.

Example 1 was repeated, except that the catalysts (of formula  $\text{Mo}_{20}\text{Ni}_{10}\text{V}_1\text{W}_1$ ) were deposited on alumina or silica in place of the silicon carbide. The results are shown in Table 5.

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TABLE 4

Example No.	Catalyst	Conversion of methacrolein (%)	Selectivity to methacrylic acid (%)	One-pass yield of methacrylic acid (%)
22	$\text{Mo}_2\text{Ni}_{10}\text{V}_1\text{W}_1\text{Li}_{10}\text{Ti}_{10}\text{O}_{22}$	67.2	73.3	49.3
23	.. $\text{NaO}_2\text{Co}_1$	67.3	67.1	45.2
24	.. $\text{K}_2\text{O}_2\text{In}_1$	66.9	69.4	46.4
25	.. $\text{K}_2\text{O}_2\text{Ti}_{10}\text{O}_{22}$	68.5	74.0	50.7
26	.. $\text{RbO}_2\text{Nb}_1$	70.8	65.7	46.5

TABLE 5

Example No.	Carrier	Conversion of methacrolein (%)	Selectivity to methacrylic acid (%)	One-pass yield of methacrylic acid (%)
27	Alumina	70.3	59.0	41.5
28	Silica	69.8	57.0	39.7

## COMPARATIVE EXAMPLE 1.

A catalyst containing molybdenum, nickel and vanadium in an atomic ratio of 20:10:1 was prepared in the manner described in Example 1. Methacrolein was then oxidized using this catalyst under the reaction conditions described in Example 1. The results are shown in Table 6.

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## COMPARATIVE EXAMPLE 2.

A catalyst containing molybdenum, nickel and tungsten in an atomic ratio 20:10:1 was prepared in the manner described in Example 1 and was used to oxidize methacrolein under the same reaction conditions as are described in Example 1. The results are shown in Table 6.

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TABLE 6

Comparative Example No.	Catalyst	Conversion of methacrolein (%)	Selectivity to methacrylic acid (%)	One-pass yield of methacrylic acid (%)
1	$\text{Mo}_2\text{Ni}_{10}\text{V}_4$	64.2	47.2	30.3
2	$\text{Mo}_2\text{Ni}_{10}\text{W}_4$	45.6	56.4	25.7

## WHAT WE CLAIM IS:—

1. A process for the preparation of methacrylic acid by the gas phase oxidation of methacrolein with molecular oxygen in the presence, as catalyst, of a composition comprising a compound oxide of molybdenum, nickel, vanadium and tungsten.
2. A process according to Claim 1, in which said oxide additionally comprises one or more of the alkali metals lithium, sodium, potassium, rubidium and caesium.
3. A process according to Claim 2, in which said oxide additionally comprises one or more of the metals, thallium, zirconium, chromium, cobalt, iron, niobium, titanium, zinc, indium and tantalum.
4. A process according to Claim 1, in which the atomic ratio  $\text{Mo:Ni:V:W:M:X}$  in said oxide is 20:1 — 20:0.1 — 10:0.1 — 10:0 — 5:0 — 10, wherein M represents one or more of the alkali metals, lithium, sodium, potassium, rubidium and caesium, and X represents one or more of the metals, thallium, zirconium, chromium, cobalt, iron, niobium, titanium, zinc, indium and tantalum.
5. A process according to Claim 4, in which said ratio is 20:7 — 13:0.5 — 2:0.5 — 2:0 — 0.5:0 — 2.
6. A process according to any one of Claims 2, 4 and 5, in which said alkali metal is potassium, rubidium or caesium.
7. A process according to any one of the preceding claims, in which said composition additionally comprises a carrier on which is deposited said compound oxide.
8. A process according to Claim 7, in which said carrier is silicon carbide, alumina or silica.
9. A process according to claim 7 or claim 8, in which from 1 to 1000 parts by weight of said compound oxide are deposited on 100 parts by weight of said carrier.
10. A process according to any one of the preceding claims, in which said compound oxide has been calcined in an air stream at a temperature of from 300° C. to 700° C. for a period of from 2 to 40 hours.
11. A process according to Claim 10, in which said temperature is from 350° C. to 600° C. and said period is from 5 to 20 hours.
12. A process according to any one of the preceding Claims, effected in the additional presence of steam.
13. A process according to Claim 12, in which the molar ratio of methacrolein to steam is from 1:1 to 1:50.

14. A process according to Claim 13, in which said molar ratio is from 1:3 to 1:30.
15. A process according to any one of the preceding Claims, effected in the additional presence of an inert gas.
16. A process according to Claim 15, in which said molecular oxygen is supplied in the form of air.
17. A process according to any one of the preceding Claims, in which the molar ratio of methacrolein to molecular oxygen is from 1:0.5 to 1:5.0.
18. A process according to Claim 17, in which the molar ratio of methacrolein to molecular oxygen is from 1:1 to 1:4.
19. A process according to any one of the preceding Claims, effected at a temperature of from 250° C. to 500° C.
20. A process according to Claim 19, in which said temperature is from 300° C. to 400° C.
21. A process according to any one of the preceding Claims effected at atmospheric pressure.
22. A process according to any one of the preceding Claims, in which the contact time of said methacrolein with said catalyst is from 0.1 to 20 seconds.
23. A process according to Claim 22, in which said contact time is from 1 to 10 seconds.
24. A process according to Claim 1, substantially as hereinbefore described with reference to any one of the foregoing Examples 1 to 28.
25. Methacrylic acid when produced by a process according to any one of the preceding claims.

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